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Source identification of water-soluble organic aerosols at a roadway site using a positive matrix factorization analysis

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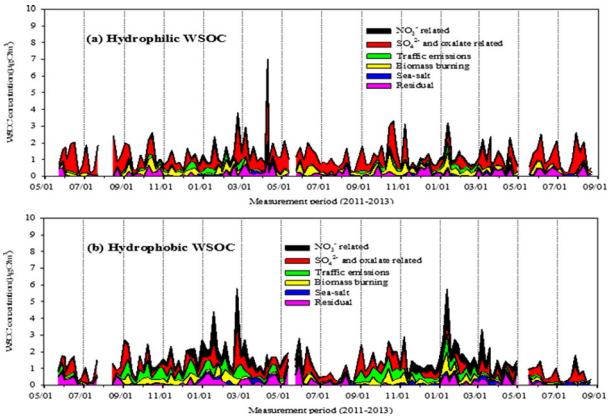
HIGHLIGHTS

- Long-term measurements of water-soluble organic carbon (WSOC) at a roadway site
- Higher fraction of hydrophilic WSOC observed in warm season
- PMF applied to elucidate sources of hydrophilic and hydrophobic WSOC
- SOA is the most dominant contributor of hydrophilic and hydrophobic WSOC.
- Biomass burning had a more significant influence on the hydrophilic WSOC.

GRAPHICAL ABSTRACT



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ABSTRACT

Daily $PM_{2.5}$ measurements were carried out at a local roadway every sixth day from May 2011 to August 2013 to obtain seasonal quantitative information on the primary and secondary sources of two water-soluble organic carbon (WSOC) fractions. Filter samples were analyzed for OC, elemental carbon (EC), WSOC, hydrophilic and hydrophobic WSOC fractions ($WSOC_{HPI}$ and $WSOC_{HPO}$), and ionic species. An XAD solid phase extraction method and a total organic carbon analyzer were used to isolate the two WSOC fractions and determine their amounts, respectively.

The WSOC/OC and $WSOC_{HPI}$/WSOC ratios were 0.62 ± 0.13 and 0.47 ± 0.14, respectively. Similar seasonal profiles in EC, OC, and WSOC concentrations were observed, with higher concentrations occurring in the cold season and lower concentrations in the warm season. However, opposite results were obtained in WSOC/OC and $WSOC_{HPI}$/WSOC ratios, with the higher in the warm season and the lower in the cold season. Correlation analyses indicated that two WSOC fractions in winter were likely attributed to secondary formation processes, biomass burning (BB), and traffic emissions, while $WSOC_{HPI}$ observed in other seasons were associated with secondary formation processes similar to those of oxalate and secondary inorganic species.

A positive matrix factorization (PMF) model was employed to investigate the sources of two WSOC fractions. PMF indicated that concentrations of WSOC fractions were affected by five sources: secondary NO_3^- related, secondary SO_4^{2-} and oxalate related, traffic emissions, BB emissions, and sea-salt. Throughout the study period, secondary organic aerosols were estimated to be the most dominant contributor of WSOC fractions, with higher

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contributions occurring in the warm seasons. The contribution of secondary aerosol formation processes (NO_3^- related + SO_4^{2-} and oxalate related) to $WSOC_{HPI}$ and $WSOC_{HPO}$ was on an average 56.2% (45.0–73.8%) and 47.7% (39.6–52.1%), respectively. The seasonal average contribution of $WSOC_{HPI}$ and $WSOC_{HPO}$ attributed to BB was 19.0% (14.3–25.3%) and 14.8% (7.2–19.5%), respectively, with higher fractions occurring in the fall and winter. Traffic sources contributed to $WSOC_{HPI}$ and $WSOC_{HPO}$ from 4.2 to 21.0% (an average of 11.6%) and from 7.9 to 32.3% (an average of 19.9%), respectively, with higher fractions in the fall and winter compared with the other seasons. During the study period, for an episode associated with high local O_3 level (~110 ppbv) and high $WSOC_{HPI}$/WSOC (0.80), secondary formation processes contributed 67.1% to $WSOC_{HPI}$, and 72.6% to $WSOC_{HPO}$, respectively. However, for an episode associated with local and severe regional haze pollutions, contributions of secondary formation processes to WSOC fractions were observed to be low (32.4–43.1%), while traffic and BB emissions contributed 16.8% and 24.3% to $WSOC_{HPI}$, respectively, and 18.3% and 18.7% to $WSOC_{HPO}$, respectively. The PMF results suggest that the contribution of traffic emissions to concentrations of two WSOC fractions cannot be neglected at the studied roadway site.

1. Introduction

Organic aerosols, which are a major component of fine particulate matter (Sillanpää et al., 2005) and rather poorly understood (Kanakidou et al., 2005), may influence the earth's radiative forcing directly by scattering light or indirectly by acting as cloud condensation nuclei (Novakov and Penner, 1993; Saxena et al., 1995; Facchini et al., 1999). Organic material is classified into two fractions, namely water-insoluble organic carbon (WIOC) and water-soluble OC (WSOC). WIOC is mainly emitted from the combustion of fossil fuels (Simoneit et al., 2004), and it consists of alkanes, alkanals, alkanons, waxes, proteins, plant fragments, and small living organisms (Pöschl, 2005). WSOC is a complex mixture of many functional groups of compounds. It is emitted directly from combustion sources, and is formed by the gas-to-particle conversion processes (Seinfeld and Pandis, 2006). Biomass burning (BB) is a significant primary source of WSOC (Saarikoski et al., 2008; Zhang et al., 2010; Du et al., 2014; Yu et al., 2014; Kuang et al., 2015). WSOC is often considered a proxy for secondary organic aerosols (SOA) due to its highly oxidized nature (Weber et al., 2007; Park et al., 2013a; Yu et al., 2014; Kuang et al., 2015). In addition to BB emissions and SOA, traffic emissions are known primary sources of particulate WSOC (Ruellan and Cachier, 2001; Ho et al., 2006; Saarikoski et al., 2008; Cho and Park, 2013; Park et al., 2013a). However, their contribution differs significantly depending on the season and the location. Some researchers performed a positive matrix factorization (PMF) model to estimate the contributions of sources to WSOC. In Helsinki, Finland (Saarikoski et al., 2008), WSOC was significantly attributed to SOA (48%), with the highest contribution (78%) in summer and the lowest (28%) in winter. In addition, the contributions of BB and traffic emissions to WSOC were found to be 17.3% (2.3% in summer to 38% in winter) and 12.9% (6.6% in summer to 16% in winter), respectively. In the southeastern United States, the contribution of BB emissions to WSOC was annually 14%. The contribution to WSOC was strongly associated with secondary aerosol formation processes, with an average of 78% (Zhang et al., 2010). In addition, the contributions of BB and secondary processes to WSOC in Beijing, China, were estimated to be about 40% and 54%, respectively (Du et al., 2014). However, BB emissions in coastal area in Shenzhen, China, were found to be the most significant contributor to the droplet mode WSOC (1.0–1.8 μm) in both the summer (68%) and the winter (87%) (Huang et al., 2006). In an urban area in Gwangju, Korea, secondary formation processes were, on an average, estimated to contribute 38% to WSOC in $PM_{2.5}$ in winter (Cho and Park, 2013). The results of previous studies indicate that source contributions of WSOC differ significantly depending on the season and location.

Based on solid-phase extraction methods, the WSOC can be further classified into more hydrophilic (soluble) and more hydrophobic (less soluble) components (Duarte and Duarte, 2005; Graber and Rudich, 2006; Sullivan and Weber, 2006; Park et al., 2012a, 2013a). A number of studies based on the sub-classification of WSOC have been conducted to investigate the chemical evolution of SOA. Fresh WSOC observed when photochemical activity was enhanced contained higher fractions of hydrophilic WSOC, which is from SOA (Sullivan and Weber, 2006; Park et al., 2013a; Yu et al., 2014), while higher fractions of hydrophobic WSOC were emitted from combustion sources such as BB, motor vehicles and coal burning (Yu et al., 2004; Yang et al., 2005; Sullivan and Weber, 2006; Lin et al., 2010; Park et al., 2012b, 2013a) or they were associated with long-range transported aerosols (Miyazaki et al., 2009; Park et al., 2012c). However, Kuang et al. (2015) indicated that traffic emissions were not a contributor to HULIS (humic-like substances, hydrophobic fraction of WSOC), but were an important source of hydrophilic WSOC at an urban site and a suburban site in the Pearl River Delta (PRD), China. Also BB was a significant contributor to HULIS with strong seasonal variations.

Results from our previous studies which were performed for the limited sampling periods at a roadway site suggest that traffic emissions were likely an important source of total WSOC and two fractionated WSOC during winter, but this is not the case during summer. Also BB emissions were a significant contributor to total WSOC and hydrophilic WSOC, but in the case of hydrophobic WSOC, the influence of BB was found to be negligible and still uncertain. In sum, the influence of primary combustion emissions (traffic and BB emissions) to total WSOC or two WSOC fractions at the roadway site was inconsistent with the results from other studies (Sullivan and Weber, 2006; Kuang et al., 2015). Due to reasons above, long-term measurements of WSOC fractions have been required to obtain more exact results on seasonal variations of the underlying primary combustion sources or formation processes of two WSOC fractions and to provide the accumulative knowledge of WSOC aerosol sources at roadway sites. In this study, an extensive data set of 24-hr $PM_{2.5}$ was generated at a roadway site every 6th day from May 2011 through August 2013. The aim of this study was to quantify the seasonal and daily source contributions of two WSOC fractions using PMF analysis. The differences in the impacts of sources to WSOC fractions during periods of $PM_{2.5}$ episodes are also discussed. This study represents a significant contribution to the current knowledge on the sources and seasonal behavior of WSOC fractions at a site close to a roadway in an urban area.

2. Experimental section

2.1. $PM_{2.5}$ measurements

In this study, 24-hr integrated $PM_{2.5}$ samples were collected on the rooftop of a three-story building (54.3 m above sea level) on the campus of Chonnam National University (35°11′N, 126°54′E) in Gwangju, Korea. The sampling site is located approximately 70 m from a busy roadway, 0.5–0.6 km southwest of a major express highway, and surrounded by commercial and residential areas. There are large areas of rural land about 9.0 km northwest of the study site, and agricultural waste is occasionally burned in the fields between October and June. This burning of waste leads to severe problem of air pollution in Gwangju,